1   Legacy and Emerging Perfluoroalkyl Substances Are Important

2   Drinking Water Contaminants in the Cape Fear River Watershed of

3   North Carolina

4   ~~Legacy and emerging perfluoroalkyl substances are important drinking~~

5   ~~water contaminants in the Cape Fear River Watershed of North Carolina~~

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31 **Abstract**

32 Long-chain per- and polyfluoroalkyl~~perfluoroalkyl~~ substances (PFASs) are being replaced by

33 short-chain PFASs and fluorinated alternatives. For ten ~~traditionally studied~~legacy PFASs and

34 seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs), we report (1)

35 occurrence in the Cape Fear River (CFR) watershed, (2) fate in ~~drinking~~ water treatment

36 processes, and (3) adsorbability on powdered activated carbon (PAC). In the headwater region of

37 the CFR basin, PFECAs were not detected in ~~the~~ raw water of a drinking water treatment plant

38 (DWTP), but concentrations of legacy ~~traditionally studied~~ PFASs were high. The US

39 Environmental Protection Agency's lifetime health advisory level (70 ng/L) for perfluorooctane

40 sulfonic acid and perfluorooctanoic acid (PFOA) was exceeded on 57 of 127 sampling days. In

41 raw water of a DWTP downstream of a PFAS manufacturer, the mean concentration of

42 perfluoro-2-propoxypropanoic acid (PFPrOPrA), a replacement for PFOA, was 631 ng/L (n=37).

43 Six other PFECAs were detected with three exhibiting chromatographic peak areas up to 15

44 times that of PFPrOPrA. At this DWTP, PFECA removal by coagulation, ozonation,

45 biofiltration, and disinfection was negligible. PFAS adsorbability on PAC increased with

46 increasing chain length. Replacing one CF_2 group with an ether oxygen decreased PFAS affinity

47 for PAC, while replacing ~~replacement of~~ additional CF_2 groups ~~with ether oxygens~~ did not lead

48 to further affinity changes.

49

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50 ~~Table of Contents Graphic~~

∑ PFASs = 355 ng/L

∑ PFASs = 62 ng/L

∑ PFASs = 710 ng/L

PFPrOPrA / "GenX"

51

Introduction

52

53 Per- and polyfluoroalkyl substances (PFASs) are extensively used in the production of plastics,

54 water/stain repellents, firefighting foams and food-contact paper coatings. The widespread

55 occurrence of PFASs in drinking water sources is closely related to the presence of point-sources

56 such as industrial sites, military fire training areas, civilian airports, and wastewater treatment

57 plants.[1] Until 2000, long-chain perfluoroalkyl sulfonic acids ($C_nF_{2n+1}SO_3H$, $n \geq 6$, PFSAs) and

58 perfluoroalkyl carboxylic acids ($C_nF_{2n+1}COOH$, $n \geq 7$, PFCAs) long-chain PFASs, such as

59 perfluorocarboxylic acids (PFCAs) with 7 or more carbon atoms and perfluorosulfonic acids

60 (PFSAs) with 6 or more carbon atoms, were predominantly used.[2] Accumulating evidence about

61 ecotoxicological the ecological persistence and human health effects[3,4] associated with exposure

62 to long-chain PFASs[3,4] has led to increased regulatory attention. Recently the U.S.

63 Environmental Protection Agency (USEPA) established a lifetime health advisory level (HAL)

64 of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid

65 (PFOS) concentrations in drinking water.[5,6] Over the last decade, production of long-chain

66 PFASs has declined in Europe and North America, and manufacturers are moving towards short-

67 chain PFASs and fluorinated alternatives.[7-10] Some fluorinated alternatives were recently

68 identified,[8,11] but others remain unknown[12-14] because they are either proprietary or

69 manufacturing byproducts.

70 One group of fluorinated alternatives, perfluoroalkyl ether carboxylic acids (PFECAs), was

71 recently discovered in the Cape Fear River (CFR) downstream of a PFAS manufacturing

72 facility.[11] Identified PFECAs included perfluoro-2-methoxyacetic acid (PFMOAA), perfluoro-3-

73 methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoro-

74 2-propoxypropanoic acid (PFPrOPrA), perfluoro(3,5-dioxahexanoic) acid (PFO2HxA),

75 perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA) and perfluoro(3,5,7,9-tetraoxadecanoic) acid

76 (PFO4DA) (Table S1 and Figure S1 in supporting information (SI)). The ammonium salt of

77 PFPrOPrA is a known PFOA alternative[13] that has been produced since 2010 with the trade

78 name "GenX".[15] According to the manufacturer, the ether oxygen enables "very rapid

79 bioelimination"[15], however, eExcept for the very few studies (most by the

80 manufacturer)PFPrOPrA data reported by the manufacturer,[16-20] little information is available

81 unknown about the pharmacokinetic behavior, toxicity, or environmental fate and transport of

82 PFECAs. To the knowledge of the authors, the only other published PFECA occurrence data are

83 for PFPrOPrA in Europe and China,[21] and no published data are available on the fate of PFECAs

84 during water treatment.

85 The strong C-F bond makes PFASs refractory to abiotic and biotic degradation,[22] and most water

86 treatment processes are ineffective for legacy PFAS removal.[23-28] Processes capable of removing

87 PFCAs and PFSAs include nanofiltration,[29] reverse osmosis[26], ion exchange,[29, 30] and activated

88 carbon adsorption,[29, 30] with activated carbon adsorption being the most widely employed

89 treatment option.

90 The objectives of this research were to (1) identify and quantify the presence of legacy PFASs

91 and emerging PFECAs in drinking water sources, (2) assess PFAS removal by conventional and

92 advanced processes in a full-scale drinking water treatment plant (DWTP), and (3) evaluate

93 PFAS adsorbability by powdered activated carbon (PAC).

Materials and Methods

95 **Water samples**: Source water of three DWTPs treating surface water in the CFR watershed was

96 sampled between June 14 and December 2, 2013 (Figure S2 in SI). Samples were collected from

97 the raw water tap at each DWTP daily as either 8-hour composite (DWTP A, 127 samples) or

98 24-hour composite (DWTP B, 73 samples; DWTP C, 34 samples). Samples were collected in

99 250-mL HDPE bottles and picked up (DWTPs A and B) or shipped overnight (DWTP C) on a

100 weekly basis. All samples were stored at room temperature until analysis (within 1 week of

101 receiving receipt). PFAS losses during storage were negligible based on results of a 70-day

102 holding study at room temperature. On August 18, 2014, grab samples were collected at DWTP

103 C after each unit process in the treatment train (raw water ozonation,

104 coagulation/flocculation/sedimentation, settled water ozonation, biological activated carbon

105 (BAC) filtration, disinfection by medium pressure UV lamps and free chlorine). Operational

106 conditions of DWTP C on the sampling day are listed in Table S2 in SI. Samples were collected

107 in 1-L HDPE bottles and stored at room temperature until analysis. On the same day, grab

108 samples of CFR water were collected in six 20-L HDPE carboys at William O. Huske Lock and

109 Dam downstream of a PFAS manufacturing site and stored at 4°C until use in PAC adsorption

110 experiments (). Background water matrix characteristics are summarized in Table S3 in SI.

111 **Adsorption experiments**: PFAS adsorption by PAC was studied in batch reactors (amber glass

112 bottles, 0.45 L CFR water). PFECA adsorption was studied at ambient concentrations (~1,000

113 ng/L PFPrOPrA, chromatographic peak areas of other PFECAs ~10-800% of the PFPrOPrA

114 area). Legacy PFASs were present at low concentrations (<40 ng/L) and spiked into CFR water

115 at ~1000 ng/L each. Data from spiked and non-spiked experiments showed that the methanol

116 contribution (1 ppm) from the primary stock solution and the added legacy PFASs 1 ppm, did

117 not affect native PFECA removal. ~~Background water matrix characteristics are summarized in~~

118 ~~Table S3 in SI.~~ A thermally-activated, wood-based PAC (PicaHydro MP23, PICA USA,

119 Columbus OH, mean diameter: 12 μm, BET surface area: 1460 m^2/g)[31] proved effective for

120 PFAS removal in a prior study[30] was used at doses of 30, 60 and 100 mg/L. These doses

121 represent the upper feasible end for drinking water treatment. Samples were taken prior to and

122 periodically after PAC addition for PFAS analysis. PFAS losses in PAC-free blanks were

123 negligible.

124 **PFAS analysis:** Information about analytical standards and ~~the~~ liquid chromatography-tandem

125 mass spectrometry (LC-MS/MS) method~~s~~ for PFAS quantification is provided in ~~SI~~the

126 supporting information.

127 **Results and Discussion**

128 **PFAS occurrence in drinking water sources**: Mean PFAS concentrations in source water of

129 three DWTPs treating surface water from the CFR watershed are shown in Figure 1. In

130 communities A and B, only legacy PFASs were detected (mean $\sum$PFAS: 355 ng/L in community

131 A, 62 ng/L in community B). Detailed concentration data are shown in Table S6 and Figure S3

132 ~~in SI~~. In community A, PFCAs with 4-8 total carbons, perfluorohexane sulfonic acid (PFHxS)

133 and PFOS were detected at median concentrations > QLs. ~~Mean and median concentrations were~~

134 ~~44 and 29 ng/L, respectively, for PFOS, and 46 and 34 ng/L, respectively, for PFOA.~~ During the

135 127-day sampling campaign, the sum concentration of PFOA and PFOS exceeded the USEPA

136 HAL of 70 ng/L on 57 days~~, and t~~The mean sum concentration of PFOA and PFOS over the

137 entire study period was 90 ng/L with approximately equal contributions of PFOS (44 ng/L) and

138 PFOA (46 ng/L). Maximum PFOS and PFOA concentrations were 346 and 137 ng/L,

139 respectively. Similar ~~legacy PFAS~~PFOS and PFOA concentrations were observed in the same

140 area ten-years-ago in 2006,[32] suggesting that PFAS source(s) upstream of community A have

141 continued long-term negative impacts on drinking water quality. Also, our data show that legacy

142 PFASs remain as surface water contaminants of concern even though their production has

143 beenwas recently phased out in the US. It is important to note, however, that the contribution of

144 long-chain PFCAs to ΣPFAS shifted from long-chain (70% $C_nF_{2n+1}COOH$, $n \geq 7$) in 2006 to short-

145 chain (70% $C_nF_{2n+1}COOH$, $n=3-6$) in 2013. In contrast, the PFOS contribution to ΣPFAS

146 remained the same (13%). Relating total PFAS concentration to average daily stream flow

147 (Figure S4 in SI) illustrated a general trend of low PFAS concentrations at high flow and high

148 concentrations at low flow, consistent with the hypothesis of upstream point source(s).

149

150 In community B, perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA) were the

151 most frequently detected, with mean concentrations of 12 and 19 ng/L, respectively. Mean and

152 median PFOA and PFOS concentrations were <QL, and the maximum sum concentration of

153 PFOA and PFOS was 59 ng/L. Lower PFAS concentrations in community B relative to

154 community A can be explained by the absence of substantive PFAS sources between the two

155 communities, dilution by tributaries, and the buffering effect of Jordan Lake, a large reservoir

156 located between communities A and B.
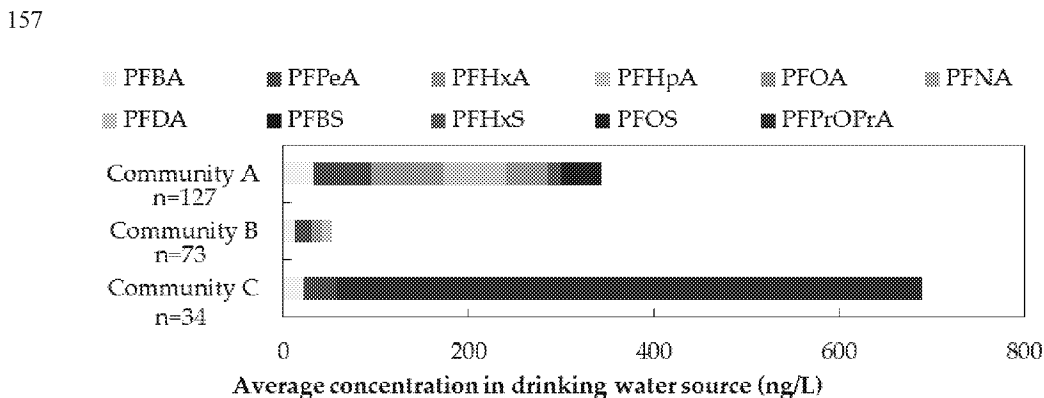
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158

159 Figure 1. PFAS occurrence at drinking water intakes in the CFR watershed. Concentrations

160 represent averages of samples collected between June and December 2013. Individual samples

161 with concentrations < QLs were considered as 0 when calculating averages, and average

162 concentrations < QLs were not plotted.

163

164

165 In community C (downstream of a PFAS manufacturing site), ~~legacy PFAS concentrations were~~

166 ~~low, and~~ only mean ~~(and median)~~ concentrations of PFBA and PFPeA were >QLs. The relatively

167 low concentrations of legacy PFASs in the finished drinking water of community C are

168 consistent with data reported from this DWTP in the third unregulated contaminant monitoring

169 rule (UCMR3) conducted by USEPA.[33] However, high concentrations of PFPrOPrA were

170 detected (up to ~4500 ng/L). The average PFPrOPrA concentration (631 ng/L) was

171 approximately eight times the average summed PFCA and PFSA concentrations (79 ng/L). Other

172 PFECAs had not yet been identified at the time of analysis. Similar to communities A and B, the

173 highest PFAS concentrations for community C were also observed at low flow (Figure S3 ~~in SI~~).

174 Stream flow data were used in conjunction with PFPrOPrA concentration data to determine

175 PFPrOPrA mass fluxes at the DWTP intake of community C. Daily mass fluxes ranged from 0.6-

176 24 kg PFPrOPrA/d with a mean value of 5.9 kg PFPrOPrA/d.

177

178 **PFAS fate in conventional and advanced water treatment processes**: To investigate whether

179 PFASs can be removed from impacted source water, samples from DWTP C were collected at

180 the intake and after each treatment step. Results in Figure 2 suggest conventional and advanced

181 treatment processes (coagulation/flocculation/sedimentation, raw and settled water ozonation,

182 BAC filtration, disinfection by medium pressure UV lamps and free chlorine) did not remove

183 legacy PFASs, consistent with previous studies.[23-27] The data further illustrate that no measurable

184 PFECA removal occurred in this DWTP. Concentrations of some PFCAs, PFSAs, PFMOPrA,

185 PFPrOPrA and PFMOAA may have increased after ozonation, possibly due to the oxidation of

186 precursor compounds.[26] Disinfection with medium pressure UV lamps and free chlorine (located

187 the between BAC effluent and the finished water) may have decreased concentrations of

188 PFMOAA, PFMOPrA, PFMOBA and PFPrOPrA, but only to a limited extent. Alternatively,

189 small concentration changes between treatment processes may be related to temporal changes in

190 source water PFAS concentrations that occurred in the time frame corresponding to the hydraulic

191 residence time of the DWTP.

192 Results in Figure 2 further illustrate that the PFAS signature of the August 2014 samples was

193 similar to the mean PFAS signature observed during the 2013 sampling campaigns shown in

194   Figure 1; i.e., PFPrOPrA concentrations (400-500 μgng/L) greatly exceeded legacy PFAS

195   concentrations. Moreover, three PFECAs (PFMOAA, PFO2HxA and PFO3OA)[11] had peak areas

196   2-113 times greater than that of PFPrOPrA (Figure 2b). The existence of high levels of emerging

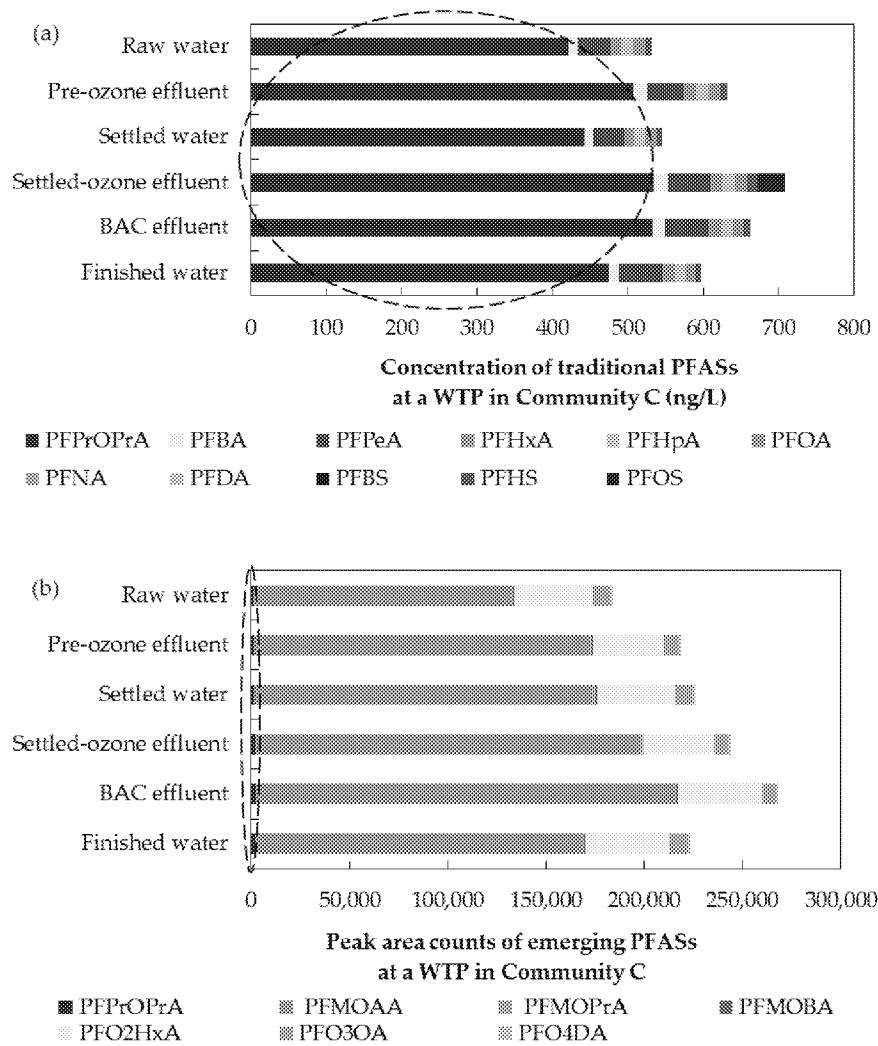197   PFASs suggests the necessity of incorporating them into routine monitoring.

198

(a)

Concentration of traditional PFASs
at a WTP in Community C (ng/L)

■ PFPrOPrA   PFBA   ■ PFPeA   ▨ PFHxA   ▧ PFHpA   ▨ PFOA
▨ PFNA   ▨ PFDA   ■ PFBS   ■ PFHS   ■ PFOS

(b)

Peak area counts of emerging PFASs
at a WTP in Community C

■ PFPrOPrA   ▨ PFMOAA   ▨ PFMOPrA   ■ PFMOBA
   PFO2HxA   ▨ PFO3OA   ▨ PFO4DA

199

200 **Figure 2.** Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water

201 treatment plant. Because authentic standards were not available for emerging PFECAs,

202 chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both

203 panels and highlighted in dashed ovals for reference. Compounds with concentrations <QL were

204 not plotted.

205

206 **PFAS adsorption by PAC**: PAC can effectively remove long-chain PFCAs and PFSAs, but its

207 effectiveness decreases with decreasing PFAS chain length.[25, 26, 30] It is unclear, however, how

208 the presence of ether group(s) in PFECAs impacts adsorbability. After a contact time of 1 hour, a

209 PAC dose of 100 mg/L achieved >80% removal of legacy PFCAs with carbon chain length $\geq$7.

210 At a PAC dose of 60 mg/L, >80% removal was achieved for PFCAs with carbon chain length $\geq$8

211 over the same time. At a the same PAC dose of 100 mg/L, removals were 95% for PFO4DA and

212 54% for PFO3OA, but <40% for other PFECAs. Detailed removal percentage data as a function

213 of PAC contact time are shown in Figure S5 in SI. There was no meaningful removal of

214 PFMOBA and PFMOPrA, and the variability shown in Figure S5 is most likely associated with

215 analytical variabilityThere was no meaningful removal for either PFMOBA or PFMOPrA, and

216 the concentration variation was caused by the fluctuation of analytical methods. Thus, the

217 removal of both compounds should be considered zero. PFMOAA could not be quantified by the

218 analytical method used in this test; however, based on the observations that PFAS adsorption

219 decreases with decreasing carbon chain length and that PFECAs with one or two more additional

220 carbon atoms than PFMOAA (i.e., PFMOPrA and PFMOBA) were poorly adsorbedexhibited

221 negligible by PACremoval (Figure 3), it is expected that PFMOAA adsorption is also negligible

222 at the tested conditions.

223 To compare the affinity of different PFASs for PAC, the PFAS removal percentages in solution

224 were plotted as a function of PFAS chain length (the sum of carbon (including branched), ether

225 oxygen, and sulfur atoms) (Figure 3(b)). The adsorbability of both legacy and emerging PFASs

226 increased with increasing chain length. PFSAs were more readily removed than PFCAs of

227 matching chain length, which agrees with previous studies.[25, 26, 30] PFECAs exhibited lower

228 adsorbabilities than PFCAs of the same chain length (e.g. PFMOBA<PFHxA), suggesting that the

229 replacement of a CF_2 group with an ether oxygen atom decreases the affinity of PFASs for PAC.

230 However, the replacement of additional CF_2 groups with ether groups resulted in small or

231 negligible affinity changes among the studied PFECAs (e.g., PFMOBA~PFO2HxA).

232 Alternatively, if only the number of perfluorinated carbons were considered as a basis of

233 comparing adsorbability, the interpretation would be different. In that case, with the same

234 number of perfluorinated carbons, PFCAs have a higher affinity for PAC than mono-ether

235 PFECAs (e.g., PFPeA>PFMOBA), but a lower affinity than multi-ether PFECAs (e.g.,

236 PFPeA<PFO3OA).

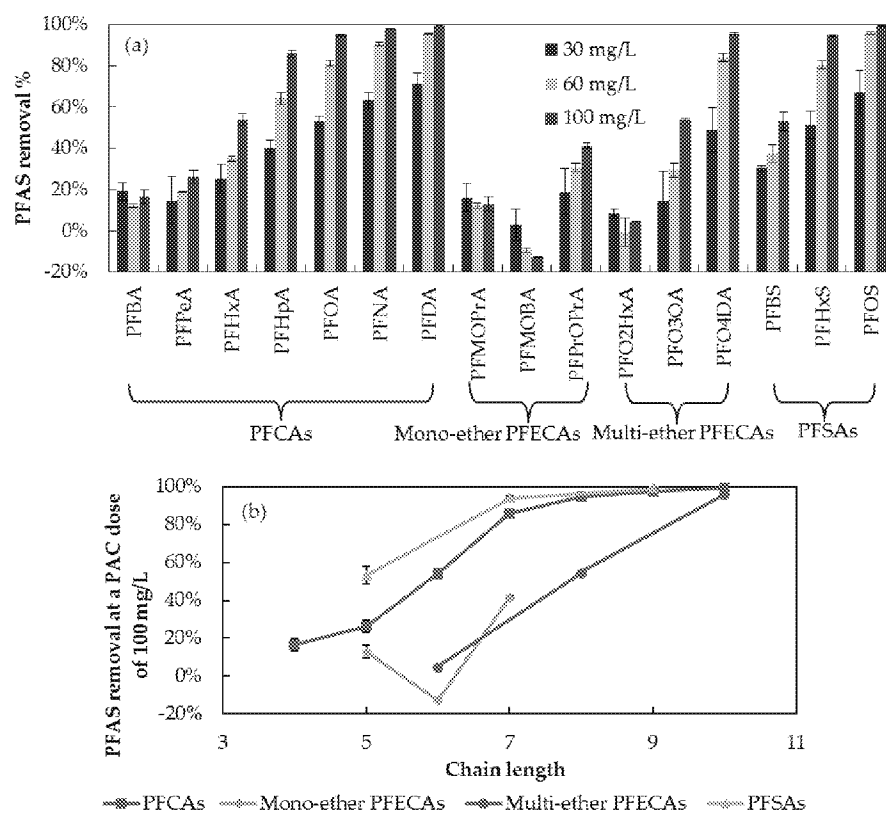Commented [DK8]: We could consider deleting this if we encounter length issues. But keep if we have the room…

237

238

239 **Figure 3.** PFAS adsorption on PAC (a) at carbon doses of 30, 60 and 100 mg/L and (b) as a

240 function of PFAS chain length. PAC contact time in CFR water was 1 hour. Legacy PFASs were

241 spiked at ~1000 ng/L and the emerging PFASs were at ambient concentrations. Figures show

242 average PFAS removal percentages, and error bars show one standard deviation of replicate

243 experiments.

244

245 In either framework, it is clear that the presence of ether groups in PFECAs changes their

246 propensity to leave the aqueous phase and adsorb on PAC. It can thus be inferred that the

247 incorporation of ether groups changes physiochemical properties, such as the octanol-water

248 partition coefficient and aqueous solubility of PFECAs relative to PFCAs. Consequently, it is

249 reasonable to expect that fate and transport of PFECAs in natural and engineered systems will

250 differ from that of legacy PFCAs. For example, while PFPrOPrA ("GenX") may be less

251 bioaccumulative than PFOA, which it is replacing, the adsorption data here suggest PFPrOPrA is

252 less hydrophobic than PFOA. Thus, when released to the environment, PFPrOPrA has a higher

253 tendency to remain in the aqueous phase and is more difficult to remove from drinking water

254 sources by adsorptive means.

255 To the knowledge of the authors, this is the first paper reporting the behavior of recently

256 identified PFECAs in water treatment processes. We further show that legacy PFASs continue to

257 be a concern in the upper reaches of the CFR basin, and that PFECAs are an important class of

258 fluorinated alternatives that dominated the PFAS signature in a drinking water source

259 downstream of a fluorochemical manufacturer and that PFECA removal by many conventional

260 and advanced treatment processes was negligible. The relatively low concentrations of legacy

261 PFASs in the finished drinking water of community C are consistent with data reported from this

262 DWTP in the third unregulated contaminant monitoring rule (UCMR3) conducted by USEPA[33].

263 Our adsorption data further show that PFPrOPrA ("GenX") is less adsorbable than PFOA, which

264 it is replacing. Thus, while the bioelimination rate of PFPrOPrA is more rapid than that of

265 PFOA, PFPrOPrA is also difficult to remove from drinking water sources by adsorptive means.

266 However, tThe detection of potentially high levels of PFECAs, the continued presence of high

267 levels of legacy PFASs, and the difficulty to in effectively removinge not only legacy PFASs but

268 also and PFECAs with many water treatment processes, suggest the need for broader discharge

269 control and contaminant monitoring.

Commented [DK9]: Could delete this. We then have to lead into the next sentence by saying: Incorporation of an ether oxygen may increase the bioelimination rate of PFPrOPrA ("GenX") relative to PFOA, which..., but it also has a higher tendency to remain in…

Commented [M10R9]: I can't think of a smooth transaction from previous paragraph to the sentence as you suggested…

270 **Acknowledgement**

273 Notes

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277

278 **Supporting Information Available**

279 The following information is available free of charge via the Internet at http://pubs.acs.org: d Six

280 tables, five figures, information about PFASs, analytical methods, and detailed results escription

281 of analytical standards and PFAS quantification, PFASs detected in the CFR watershed,

282 operational conditions of DWTP-C on sampling day, water quality characteristics of surface

283 water used in adsorption tests, LC gradient method for PFAS analysis, MS transitions for PFAS

284 Analysis, maximum, minimum, mean and median concentrations (ng/L) of PFASs in CFR

285 watershed surface water as drinking water sources, molecular structures of PFECAs in this study,

286 sampling sites in the CFR watershed, PFAS concentration distributions in the CFR watershed at

287 three drinking water intakes, total PFAS concentrations in the source water and stream flow at

288 the three studied DWTPs, and PFAS adsorption on PAC.

> **Commented [DK11]:** I shortened significantly based on other statements I have seen in ES&T Letters.

289 **Reference**

290 1.   Hu, X. C.; Andrews, D. Q.; Lindstrom, A. B.; Bruton, T. A.; Schaider, L. A.; Grandjean, P.;
291 Lohmann, R.; Carignan, C. C.; Blum, A.; Balan, S. A.; Higgins, C. P.; Sunderland, E. M.,
292 Detection of poly- and perfluoroalkyl substances (PFASs) in U.S. drinking water linked to

293   industrial sites, military fire training areas, and wastewater treatment plants. *Environ. Sci.*
294   *Technol. Lett.* **2016,** *3,* (10), 344–350.
295   2.   Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; de Voogt, P.; Jensen, A.
296   A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. J., Perfluoroalkyl and polyfluoroalkyl
297   substances in the environment: Terminology, classification, and origins. *Integr. Enviro. Assess.*
298   *Manage.* **2011,** *7,* (4), 513-541.
299   3.   Kennedy, G. L.; Butenhoff, J. L.; Olsen, G. W.; O'Connor, J. C.; Seacat, A. M.; Perkins, R.
300   G.; Biegel, L. B.; Murphy, S. R.; Farrar, D. G., The toxicology of perfluorooctanoate. *Crit. Rev.*
301   *Toxicol.* **2004,** *34,* (4), 351-384.
302   4.   D. Borg; H. Hakansson *Environmental and health risk assessment of perfluoroalkylated and*
303   *polyfluoroalkylated substances (PFASs) in sweden, Report 6513*; The Swedish Environmental
304   Protention Agency: 2012.
305   5.   US Environmental Protection Agency *Drinking water health advisory for perfluorooctanoic*
306   *acid (PFOA)* 822-R-16-005; 2016.
307   6.   US Environmental Protection Agency *Drinking water health advisory for perfluorooctane*
308   *sulfonate (PFOS)* 822-R-16-004; 2016.
309   7.   Scheringer, M.; Trier, X.; Cousins, I. T.; de Voogt, P.; Fletcher, T.; Wang, Z.; Webster, T.
310   F., Helsingør Statement on poly- and perfluorinated alkyl substances (PFASs). *Chemosphere*
311   **2014,** *114,* 337-339.
312   8.   Wang, Z.; Cousins, I. T.; Scheringer, M.; Hungerbühler, K., Fluorinated alternatives to
313   long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and
314   their potential precursors. *Environ. Int.* **2013,** *60,* 242-248.
315   9.   Wang, Z.; Cousins, I. T.; Scheringer, M.; Hungerbuehler, K., Hazard assessment of
316   fluorinated alternatives to long-chain perfluoroalkyl acids (PFAAs) and their precursors: Status
317   quo, ongoing challenges and possible solutions. *Environ. Int.* **2015,** *75,* 172-179.
318   10.   Barzen-Hanson, K. A.; Field, J. A., Discovery and implications of C2 and C3
319   perfluoroalkyl sulfonates in aqueous film-forming foams and groundwater. *Environ. Sci.*
320   *Technol. Lett.* **2015,** *2,* (4), 95-99.
321   11.   Strynar, M.; Dagnino, S.; McMahen, R.; Liang, S.; Lindstrom, A.; Andersen, E.; McMillan,
322   L.; Thurman, M.; Ferrer, I.; Ball, C., Identification of novel perfluoroalkyl ether carboxylic acids
323   (PFECAs) and sulfonic acids (PFESAs) in natural waters using accurate mass time-of-flight mass
324   spectrometry (TOFMS). *Environ. Sci. Technol.* **2015,** *49,* (19), 11622-11630.
325   12.   Miyake, Y.; Yamashita, N.; Rostkowski, P.; So, M. K.; Taniyasu, S.; Lam, P. K. S.; Kannan,
326   K., Determination of trace levels of total fluorine in water using combustion ion
327   chromatography for fluorine: A mass balance approach to determine individual perfluorinated
328   chemicals in water. *J. Chromatogr. A* **2007,** *1143,* (1–2), 98-104.
329   13.   Wagner, A.; Raue, B.; Brauch, H.-J.; Worch, E.; Lange, F. T., Determination of adsorbable
330   organic fluorine from aqueous environmental samples by adsorption to polystyrene-
331   divinylbenzene based activated carbon and combustion ion chromatography. *J. Chromatogr. A*
332   **2013,** *1295,* 82-89.
333   14.   Willach, S.; Brauch, H.-J.; Lange, F. T., Contribution of selected perfluoroalkyl and
334   polyfluoroalkyl substances to the adsorbable organically bound fluorine in German rivers and
335   in a highly contaminated groundwater. *Chemosphere* **2016,** *145,* 342-350.

336 15.   DuPont DuPont GenX processing aid for making fluoropolymer resins.
337 https://www.chemours.com/Industrial_Bakery_Solutions/en_GB/assets/downloads/Chemours_
338 GenX_Brochure_Final_07July2010.pdf (accessed July 29, 2016),
339 16.   Gannon, S. A.; Fasano, W. J.; Mawn, M. P.; Nabb, D. L.; Buck, R. C.; Buxton, L. W.;
340 Jepson, G. W.; Frame, S. R., Absorption, distribution, metabolism, excretion, and kinetics of
341 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid ammonium salt following a single
342 dose in rat, mouse, and cynomolgus monkey. *Toxicology* **2016**, *340*, 1-9.
343 17.   Hoke, R. A.; Ferrell, B. D.; Sloman, T. L.; Buck, R. C.; Buxton, L. W., Aquatic hazard,
344 bioaccumulation and screening risk assessment for ammonium 2,3,3,3-tetrafluoro-2-
345 (heptafluoropropoxy)-propanoate. *Chemosphere* **2016**, *149*, 336-342.
346 18.   Caverly Rae, J. M.; Craig, L.; Slone, T. W.; Frame, S. R.; Buxton, L. W.; Kennedy, G. L.,
347 Evaluation of chronic toxicity and carcinogenicity of ammonium 2,3,3,3-tetrafluoro-2-
348 (heptafluoropropoxy)-propanoate in Sprague–Dawley rats. *Toxicol. Rep.* **2015**, *2*, 939-949.
349 19.   Wang, J.; Wang, X.; Sheng, N.; Zhou, X.; Cui, R.; Zhang, H.; Dai, J., RNA-sequencing
350 analysis reveals the hepatotoxic mechanism of perfluoroalkyl alternatives, HFPO2 and HFPO4,
351 following exposure in mice. *J. Appl. Toxicol.* **2016**.
352 20.   Gomis, M. I.; Wang, Z.; Scheringer, M.; Cousins, I. T., A modeling assessment of the
353 physicochemical properties and environmental fate of emerging and novel per- and
354 polyfluoroalkyl substances. *Sci. Total Environ.* **2015**, *505*, 981-991.
355 21.   Heydebreck, F.; Tang, J.; Xie, Z.; Ebinghaus, R., Alternative and legacy perfluoroalkyl
356 substances: Differences between european and chinese river/estuary systems. *Environ. Sci.*
357 *Technol.* **2015**, *49*, (14), 8386-8395.
358 22.   Rayne, S.; Forest, K., Perfluoroalkyl sulfonic and carboxylic acids: A critical review of
359 physicochemical properties, levels and patterns in waters and wastewaters, and treatment
360 methods. *Journal of Environmental Science and Health, Part A* **2009**, *44*, (12), 1145-1199.
361 23.   Quiñones, O.; Snyder, S. A., Occurrence of perfluoroalkyl carboxylates and sulfonates in
362 drinking water utilities and related waters from the United States. *Environ. Sci. Technol.* **2009**, *43*,
363 (24), 9089-9095.
364 24.   Shivakoti, B. R.; Fujii, S.; Nozoe, M.; Tanaka, S.; Kunacheva, C., Perfluorinated chemicals
365 (PFCs) in water purification plants (WPPs) with advanced treatment processes. *Water Sci.*
366 *Technol. Water Supply* **2010**, *10*, (1), 87-95.
367 25.   Eschauzier, C.; Beerendonk, E.; Scholte-Veenendaal, P.; De Voogt, P., Impact of
368 treatment processes on the removal of perfluoroalkyl acids from the drinking water production
369 chain. *Environ. Sci. Technol.* **2012**, *46*, (3), 1708-1715.
370 26.   Rahman, M. F.; Peldszus, S.; Anderson, W. B., Behaviour and fate of perfluoroalkyl and
371 polyfluoroalkyl substances (PFASs) in drinking water treatment: A review. *Water Res.* **2014**, *50*,
372 318-340.
373 27.   Appleman, T. D.; Higgins, C. P.; Quiñones, O.; Vanderford, B. J.; Kolstad, C.; Zeigler-
374 Holady, J. C.; Dickenson, E. R. V., Treatment of poly- and perfluoroalkyl substances in U.S. full-
375 scale water treatment systems. *Water Res.* **2014**, *51*, 246-255.
376 28.   Merino, N.; Qu, Y.; Deeb, R. A.; Hawley, E. L.; Hoffmann, M. R.; Mahendra, S.,
377 Degradation and removal methods for perfluoroalkyl and polyfluoroalkyl substances in water.
378 *Environ. Eng. Sci.* **2016**, *33*, (9), 615-649.

379   29.   Appleman, T. D.; Dickenson, E. R. V.; Bellona, C.; Higgins, C. P., Nanofiltration and
380   granular activated carbon treatment of perfluoroalkyl acids. *J. Hazard. Mater.* **2013,** *260,* 740-746.
381   30.   Dudley, L. A.; Arevalo, E. C.; Knappe, D. R. U. *Removal of perfluoroalkyl substances by PAC*
382   *adsorption and anion exchange*; Water Research Foundation: Denver, CO, 2015.
383   31.   Dunn, S. E.; Knappe, D. R. U. *Disinfection by-product precursor and micropollutant removal*
384   *by powdered activated carbon*; Water Research Foundation: Denver, CO, 2013.
385   32.   Nakayama, S.; Strynar, M. J.; Helfant, L.; Egeghy, P.; Ye, X.; Lindstrom, A. B.,
386   Perfluorinated compounds in the Cape Fear drainage basin in North Carolina. *Environ. Sci.*
387   *Technol.* **2007,** *41,* (15), 5271-5276.
388   33.   US Environmental Protection Agency Unregulated contaminant monitoring rule 3
389   (UCMR 3). http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/ucmr3/ (accessed July 29, 2016),
390